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Aeration in Aquaria

A. L. Downing & G. A. Truesdale

Water Pollution Research Laboratory, Stevenage, Herts., England

(Text-figures 1-5)

Introduction

IT is well known that to keep fish alive and healthy in aquaria it is necessary to ensure that the water contains an adequate concentration of dissolved oxygen. This can usually be arranged without a detailed knowledge of the physical and biochemical processes governing the level of dissolved oxygen attained under given conditions. In some cases when, for instance, there are few fish in a large volume of water with a large exposed surface and containing perhaps a few green plants, there is no apparent need to provide additional aeration. In other cases all that may be required is a stream of air bubbles passed through the water. In current research on the development of tests for the toxicity of effluents to be discharged into surface waters, however, it is sometimes desirable not merely to keep fish adequately supplied with oxygen, but also, since the toxicity of certain poisons is known to depend on the level of dissolved oxygen (Downing, 1954), to keep this concentration within prescribed limits without at the same time causing undue loss of volatile constituents. This demands a more detailed knowledge of the aeration process and of the other factors affecting the concentration of dissolved oxygen.

Factors Affecting the Concentration of Dissolved Oxygen

The concentration of dissolved oxygen is determined by the relative magnitudes of the rates of supply and demand. On the one hand oxygen is consumed by the respiration of fish and plants, if these are present, and possibly, to a much lesser extent, by the bio-oxidation of metabolic products; on the other it is re-supplied to the water by absorption from the atmosphere and by the photosynthetic activity of plants. The assumption of Breder (1931) that photosynthesis has little influence on the concentration of dissolved oxygen cannot be accepted as an accurate generalization, although it is true that in many cases its role may be unimportant. The difficulty is that its influence cannot often be calculated quantitatively because of an inadequate knowledge of the rates of consumption or evolution of oxygen by fish or plants under given conditions. Nevertheless approximate average values of these rates for certain fishes and plants are known, and they may be used when applicable to predict the variation of dissolved oxygen in an aquarium. Before this can be done, however, the rate of absorption of oxygen from the air must be measured or estimated.

Absorption of Atmospheric Oxygen by Water

In quiescent conditions oxygen penetrates into water by molecular diffusion in accordance with Fick's law. In moving water this process is augmented by turbulent mixing of the surface layers with the main body of the liquid and by the creation of fresh surfaces. It is proposed to consider the aeration of aquaria in which the general level of turbulence, created by the devices used to promote aeration, by the movement of fish, and by miscellaneous minor disturbances is sufficient to maintain a sensibly uniform concentration of dissolved oxygen at all points below the outermost surface layers, which are assumed to be saturated with oxygen. It seems very probable that this condition will be approximately satisfied in most small aquaria (not deeper than, say, about 1 metre) since experience shows that, unless special precautions are taken to control vibrations and the temperature and humidity of the air above the surface, gradients in the oxygen concentration

are not detectable even in apparently stagnant water. This is largely due to "streaming" resulting from density changes caused by cooling of the surface layers by evaporation. In very large aquaria in which aeration was promoted by a stream of bubbles liberated a long way from the center of the bottom of the tank, such conditions might not apply. In this case, however, the rate of change of oxygen concentration at any point would be governed by random movement of the fish and any other incidental disturbances; since this would be largely unpredictable it will not be considered further.

For aquaria in which there is reasonably uniform mixing it is found that the rate of change of dissolved oxygen at any time, t, is directly proportional to the difference between the saturation concentration, C_s, and the concentration, C, in the water (Lewis & Whitman, 1924). That is,

$$\frac{dC}{dt} = K \ (C_s - C) \quad \text{...............................(1)}$$

and, integrating,

$$\log_e \frac{C_s}{C_s - C} = Kt \quad \text{.................................(2),}$$

where K, the over-all absorption coefficient, measures the rate of change of concentration of dissolved oxygen when the saturation deficit, $C_s - C$, is unity. K has dimensions T^{-1} and is generally expressed in reciprocal hours. Thus the increase of dissolved oxygen with time, due to aeration, follows an exponential curve, the exact form of which depends on the magnitude of the absorption coefficient (Text-fig. 1a). There is however no simple method for predicting accurately the magnitude of K from a knowledge of the physical characteristics of the system; such theories as there are demand a knowledge of hypothetical or difficultly measurable quantities such as the thickness of the stagnant film at the water surface (Lewis & Whitman, 1924), the time of exposure of freshly created surfaces (Higbie, 1935; Pasveer, 1953), or the rate of mixing of the water (Phelps, 1947). Fortunately, however, if it is assumed that the effect on the rate of aeration due to the movement of fish is negligible, as will generally be the case except perhaps in stagnant water, then the rate of aeration can be measured directly in the aquarium in their absence. This is conveniently done by measuring the dissolved oxygen at two times, t_1 and t_2,
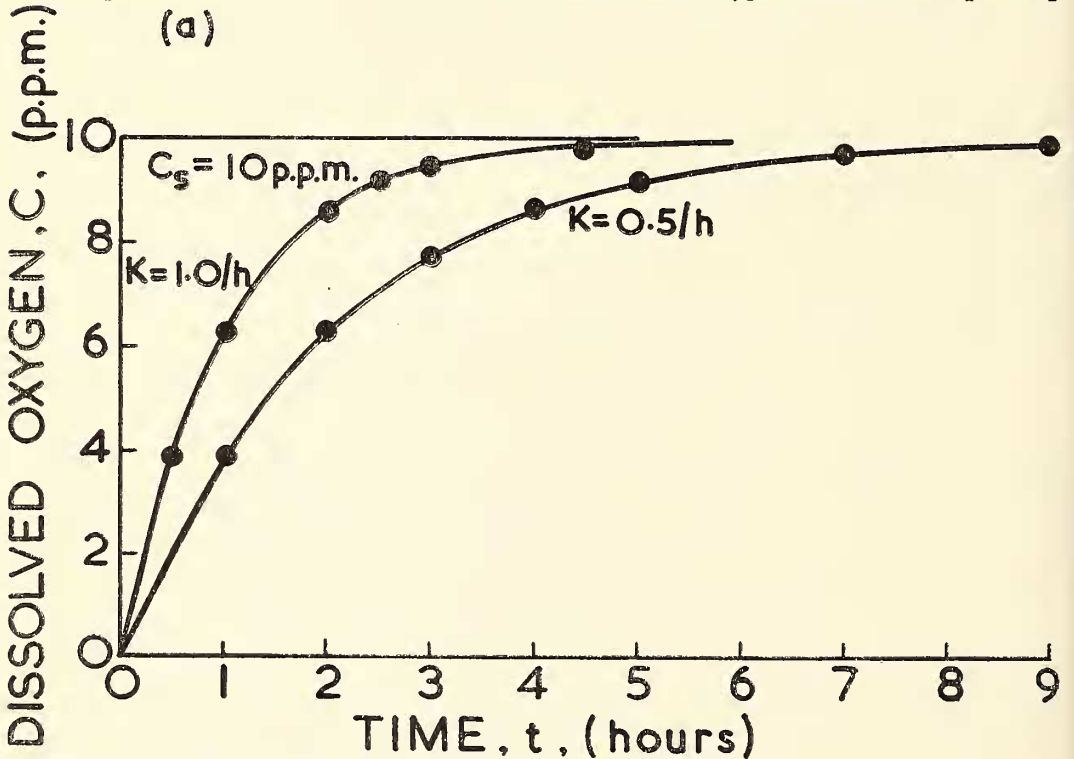
TEXT-FIG. 1(a). Rate of solution of atmospheric oxygen in water.
Temperature 13.90° C.
Solubility of oxygen, C_s, from moist air = 10 p.p.m.
Equation of absorption curves: $\log_e \dfrac{C_s}{C_s - C} = Kt.$

after partial deoxygenation of the water, followed by substitution of the values in an equation, derived from Equation (1), of the form

$$\log_e \frac{C_s - C_1}{C_s - C_2} = K(t_2 - t_1) \dots\dots\dots(3),$$

where C_1 and C_2 are the oxygen concentrations at t_1 and t_2. Alternatively K may be evaluated from the slope of the straight line obtained by plotting the logarithm of periodic observations of the saturation deficit against time. The importance of having an accurate knowledge of the solubility (Truesdale, Downing & Lowden, 1955) for these computations is demonstrated in Text-fig. 1b.

The value of K obtained in the manner indicated does however depend on the volume of water, V, and the area of the exposed surface, A, the ratio V/A being sometimes referred to as the "aeration depth." In considering the range of values in which the rate of aeration may vary under different conditions, it is therefore convenient to use a transfer coefficient, f, (sometimes called the "exit coefficient," (Gameson, Truesdale & Downing, 1955)) defined by the relation

$$K = \frac{f.A}{V}, \dots\dots\dots(4)$$

which measures the rate of change of dissolved oxygen in a unit depth of water when the saturation deficit is unity. It has dimensions LT^{-1} and is usually expressed in cm./h. It is also equivalent to the amount of oxygen passing through unit area of surface in unit time when the deficit is unity, 1cm./h. being equivalent to $1\mu g./cm.^2$, p.p.m., h. For a system having f = 10cm./h. and an aeration depth 10 cm., the over-all absorption coefficient would be 1.0/h. so that the rate of solution when the deficit was 10 p.p.m. would be 10 p.p.m./h. In making predictions of this kind it is of course tacitly assumed that the mass transfer coefficient is unaffected by changes in the aeration depth provided there is no obvious difference in the conditions of agitation at the surface from those for which the coefficient was measured. This is generally only approximately true for limited changes in V/A, and if an accurate knowledge of the rate of aeration in a particular system is required it is much safer to determine this directly in the manner indicated. The published values of mass-transfer coefficients for different aeration systems show that they are extremely dependent on the degree and type of agitation in the water and may vary between values of less than 1.0 cm./h. for stagnant water to values
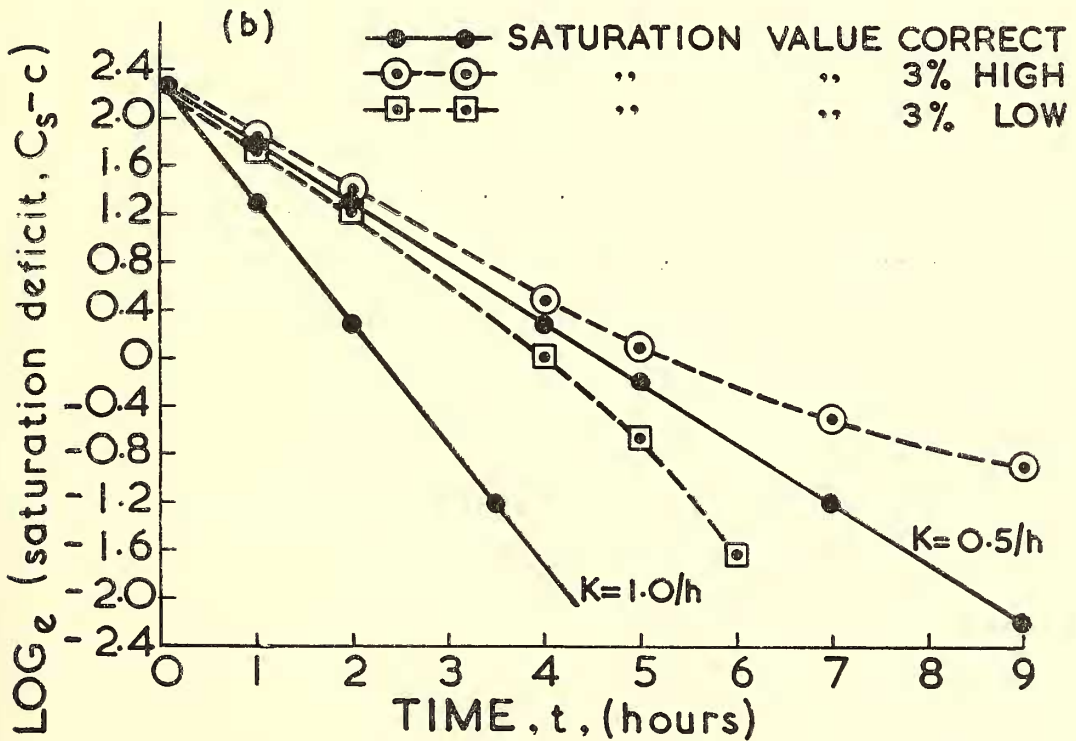
TEXT-FIG. 1(b).   Linear variation of the logarithm of the saturation deficit with time; effect of incorrect saturation values.

of the order of 500 cm./h. for rapidly stirred water (Table 1).

The mass-transfer coefficient is also dependent on the temperature, the concentration of dissolved salts, and the condition of the surface. For instance, in the temperature range 0 to 35° C., f increases by between 2.2 and 2.3 per cent. of the value at 20° C. per degree Centigrade increase in temperature (Downing & Truesdale, 1955). On the other hand it appears to be reduced by dissolved salts since the rate of solution in pure sea water and in sodium chloride solution of the same salinity is lower than that in pure water under the same conditions (Department of Scientific and Industrial Research, 1956). Soluble or insoluble surface contaminants or surface-active agents also generally cause a decrease in the rate of solution although the magnitude depends very much on their concentration and the conditions of agitation (Downing & Truesdale, 1955).

PREDICTION OF DISSOLVED OXYGEN CONCENTRATIONS IN AQUARIA

Given a knowledge of the rate of absorption of oxygen from the air and the rate of absorption or production of oxygen by respiration or photosynthesis, we are in a position to make approximate calculations of the variation of dissolved oxygen concentration with time. To simplify matters we may assume that fish and plants consume oxygen at a constant rate K_1 p.p.m./h. and K_2 p.p.m./h. respectively, and that during daylight oxygen is produced by photosynthesis at a constant rate K_3 p.p.m./h.

The rate of change of concentration of dissolved oxygen is given by

$$\frac{dC}{dt} = K(C_s - C) - K_1 - K_2 + K_3 \ldots (5)$$

and

$$\log_e \left\{ \frac{K(C_s - C_o) - K_1 - K_2 + K_3}{K(C_s - C) - K_1 - K_2 + K_3} \right\} = Kt \ldots (6),$$

so that

$$C = e^{-Kt} C_o + \frac{(1 - e^{-Kt})(KC_s - K_1 - K_2 + K_3)}{K} \ldots (7),$$

where K is the over-all absorption coefficient and C_o is the initial concentration of dissolved oxygen.

TABLE 1. OBSERVED VALUES OF THE MASS-TRANSFER COEFFICIENT, f, FOR OXYGEN IN STAGNANT AND AGITATED WATER

Description of aeration system	Approximate value or range of values taken by mass-transfer coefficient, f. (cm./h.)	Reference
Stagnant water	0.2 — 0.5	Holroyd & Parker (1952)
Slowly stirred water: no appreciable disturbance of the surface	1.0 — 5.0	Downing & Truesdale (1955)
Slowly stirred water: slight disturbance at the surface	1.0 — 10	do.
Rapidly stirred water: regular vortices at the surface	10 — 50	do.
Rapidly stirred water: irregular vortices and severely disturbed surface	*50 — 500	do.
Regular progressive waves (2.8-10.2 cm. high) in shallow water	*10 — 37	do.
"Choppy" waves (6.4-13.3 cm. high) in shallow water	*11 — 25	do.
Shallow and turbulent Lakeland beck	*30 — 200 (Depending on flow, depth, and roughness of bed)	Gameson, Truesdale & Downing (1955)
"Model Stream" flowing in channels, velocity 0.6-15 m./min.	1 — 30	Streeter, Wright & Kehr (1936)
Water surface ruffled by tangential air stream, velocity, measured near the surface, increasing to 13.5 m./sec.	1.5 — 63	Downing & Truesdale (1955)
Diffused air bubbles, 1-5 mm. in diameter	180	Holroyd & Parker (1952)
Diffused air bubbles, 2.4 mm. in diameter	Ca. 90	Scouller & Watson (1934)
Diffused oxygen bubbles, 2 mm. in diameter	96	Ippen & Carver (1954)

*Nominal values calculated using an aeration depth determined from the volume of water and the area of the undisturbed surface.

The use of this equation may be illustrated by inserting in it some typical values of the variable quantities.

Consider first the case in which no plants are present in the aquarium so that K_2 and K_3 are zero; suppose that the volume of fresh water is 100 litres with an exposed surface of 5,000 sq.cm., that this contains 10 brook trout each weighing 25 gm. and consuming oxygen at a rate of 100 ml. oxygen/Kg. fish, h., a reasonably approximate figure (Graham, 1949). Suppose further that the temperature is 13.9° C. and that the barometric pressure is 760 mm. Hg, so that the solubility of oxygen is 10 p.p.m. (Truesdale, Downing & Lowden, 1955). If no additional aeration is provided the mass transfer coefficient for the entry of oxygen through the surface will be approximately 1.0 cm./h. (Table 1). Thus

$$K = \frac{5 \times 10^3}{10^2 \times 10^3} = 0.05/h.$$

and

$$K_1 = \frac{10 \times 25}{1000} \times 100 \times 1.43 \times \frac{1}{100} =$$
$$0.36 \text{ p.p.m./h.}$$

The oxygen concentration will therefore tend to an equilibrium value given from Equation 5 when

$$\frac{dC}{dt} = 0,$$

such that

$$0.05(10-C) = 0.36$$
$$C = 2.8 \text{ p.p.m.,}$$

which is approaching a dangerously low level for trout. In theory the equilibrium concentration will be reached only after an infinite time, but if the water is initially saturated with oxygen it can be shown, by substitution in Equation (5), that a concentration within about 0.1 p.p.m. of the equilibrium value will be reached after time, t, given from Equation (6) by

$$t = \frac{1}{0.05} \log_e \left(\frac{-0.36}{(0.05)(7.1) - 0.36} \right)$$
$$= 85.5 \text{ hours}$$

and that the variation of dissolved oxygen with time will follow curve AB (Text-fig. 2). Thus even in the short space of a day, the oxygen concentration would be lowered to half its initial value.

Validity of the Theoretical Relations

At present there is little or no evidence to support the validity of the hypothetical conclusions deduced from Equations (5), (6) and (7). Some preliminary experimental studies with rainbow trout do, however, indicate that approximately correct predictions of the average concentration of dissolved oxygen in an aquarium can be made in this way (Alabaster, 1956). It is found that the oxygen concentration at any instant fluctuates about the average value between quite wide limits. This is presumably due to variations in both the rate of solution of oxygen and the oxygen consumption of the fish. If the approximate variability in these two quantities is known we can determine the probable variation in the dissolved oxygen. Thus suppose that the random variations of K and K_1 about their mean values are represented by standard errors aK, and bK_1, then the variation in the equilibrium concentration of dissolved oxygen for an aquarium containing only fish may be expressed as the standard error, σ, in the quotient K_1/K in the equation $C = C_s - K_1/K$, derived from (5), i.e., by

$$\sigma = K_1/K \sqrt{(a^2 + b^2)}.$$

Thus the variation in the equilibrium dissolved oxygen concentration will increase as K decreases or as K_1 increases; that is, it will increase as the equilibrium concentration decreases.

For instance, in the case where K = 0.05, $K_1 = 0.36$, a = b = 0.1 and $C_s = 10$, we have

$$\sigma = 7.2 \sqrt{0.02}$$
$$= 1.02$$

Thus the mean equilibrium concentration and its standard error will be 2.8 and 1.02 p.p.m. For K = 0.5,

$$\sigma = 0.72 \sqrt{0.02}$$
$$= 0.1,$$

so that in this case the error in the equilibrium concentration, C = 9.28 p.p.m., will be only 0.1 p.p.m.

Adjustment of Conditions to Satisfy Oxygen Demands

The reduction of the oxygen concentration to a dangerously low level may be prevented by (i) reducing the population of fish, (ii) decreasing the aeration depth while keeping the volume constant, (iii) increasing the partial pressure of oxygen in the gas phase, (iv) changing the water at intervals or continuously, (v) increasing the rate of absorption of oxygen from the atmosphere, or (vi) making use of photosynthesis to produce oxygen. The first two possibilities (i) and (ii) are straightforward and will not be considered further.

Increasing the partial pressure of oxygen. (iii).

This will increase the saturation concentration of oxygen in the water, in accordance with Henry's law, so that for a given deficit, $C_s - C$, the concentration of dissolved oxygen will be greater.

Replacement of water. (iv).

If, as may sometimes be the case in toxicity tests, the volume of solution available for replacement is limited and we wish to maintain the oxygen concentration between prescribed limits, the minimum frequency of periodic replacement can be ascertained by substituting the appropriate values in Equation (6). Alternatively, the rate of change of oxygen concentration that would result from replacing the water in the aquarium continuously by water, saturated with oxygen, at a rate, v litres/h., assuming rapid and complete mixing, would be given by

$$dC/dt = v/V(C_s - C) \ldots\ldots\ldots(8),$$

where V is the volume of the aquarium. Thus to maintain a given concentration, C, would require the water to be replaced at a rate given by

$$\frac{dC}{dt} = 0 = K(C_s - C) +$$

$$\frac{v}{V}(C_s - C) - K_1 - K_2 + K_3 \ldots\ldots(9)$$

so that

$$v = V\left[\frac{K_1 + K_2 - K_3}{(C_s - C)} - K\right] \ldots\ldots(10).$$

To maintain an equilibrium concentration C,

of say 6 p.p.m., when $K_1 = 0.36$ p.p.m./h. and $K_2 = K_3 = 0$, would require a rate of replacement

$$v = 100\left(\frac{0.36}{4} - 0.05\right) = 4 \text{ l./h.}$$

These rates of replacement refer only to dissolved oxygen requirements, of course. In practice other factors such as the accumulation of noxious metabolic products might necessitate more frequent replacement.

Increasing the rate of aeration. (v).

If we prefer to increase the rate of aeration, then the minimum rate required to prevent the deficit, $C_s - C$, exceeding a given value D is given by KD = 0.36, ($K_2 = K_3 = 0$). For instance, if the previous equilibrium deficit is to be reduced from 7.2 p.p.m. to say 0.72 p.p.m., then K must be increased to 5.0/h. Once K had been increased to this value the variation of oxygen concentration with time would follow curve AC (Text-fig. 2). As already indicated, this rate of aeration could be obtained in several ways; in practice the most common and easiest method is to bubble air through the water. The approximate order of frequency of bubbles and rate of flow of air required may be determined using data published in the literature. For in-
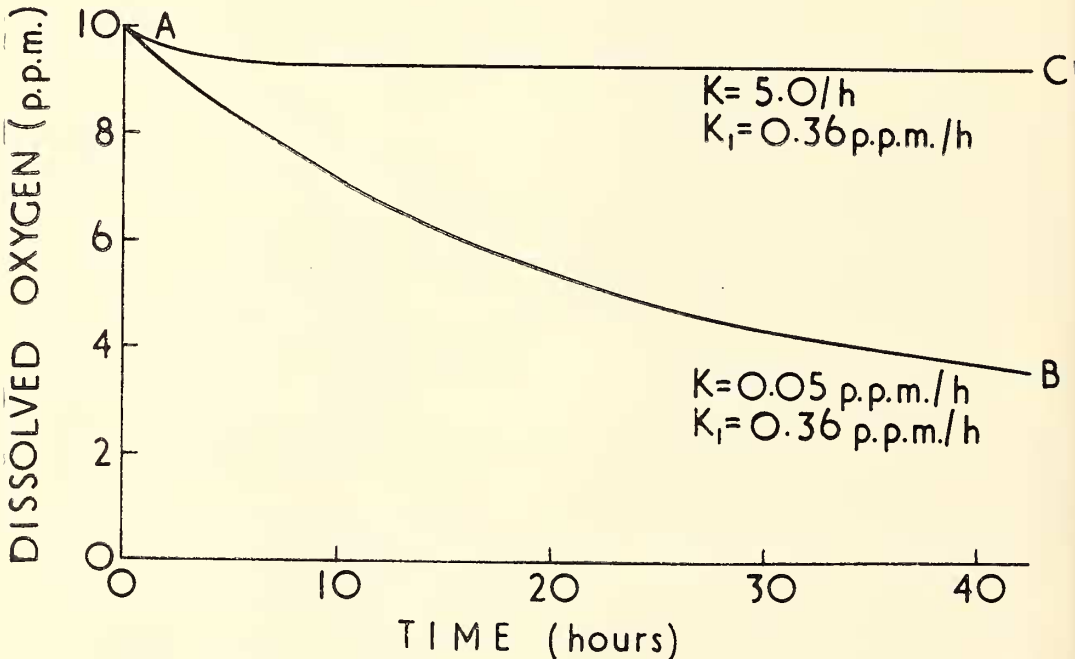
TEXT-FIG. 2. Effect of the respiration of fish on the variation of concentration of dissolved oxygen in aquaria.

K: over-all absorption coefficient.

K_1: rate of consumption of dissolved oxygen by fish.

stance the average mass-transfer coefficient for streams of bubbles (from a porous diffuser) having an average radius of about 1 to 2 mm. has been found to be of the order of 200 cm./h. (Holroyd & Parker, 1949; Datta, Napier & Newitt, 1950), so that if we wish to increase K from 0.05 to 0.50, neglecting the effect of the bubbles on the aeration at the surface, the total surface area of the bubbles that must be present instantaneously is given from Equation (4) by

$$0.45 = \frac{200 \times A}{10^2 \times 10^3}.$$

$$\therefore \quad A = 225 \text{ sq. cm.}$$

Thus if we assume for this purpose that all the bubbles have a radius of 1 mm., the total number, N, that must be instantaneously present is $225/4\pi(0.1)^2$, that is, about 1,900. If the velocity of the bubbles is for simplicity assumed to be constant at the approximate terminal velocity for this size of bubble, 20 cm./sec. (Ippen & Carver, 1954), then the required frequency of production of bubbles, F, is given by

$$F = N \times \frac{\text{depth}}{\text{velocity}} = N \times 20/20, \text{ whence}$$

$$F = 1900 \text{ bubbles/sec.}$$

This corresponds to an airflow of about 475 ml./min.

In practice, it would be necessary to make preliminary trials with diffusers of different sizes and porosities to select one that gave bubbles of the size required, since the size is found to vary with porosity, loading, and the nature of the liquid.

It will of course be appreciated that this simple treatment neglects many factors such as the variation with depth of water of the bubble size and velocity as well as the partial pressure of oxygen within the bubble and hence of the saturation concentration of oxygen at the bubble interface. An interesting and more rigorous treatment of this subject is given by Pasveer (1954).

Production of oxygen by photosynthesis. (vi).

When living aquatic plants containing chlorophyll are illuminated, oxygen is produced by photosynthesis as a result of a complex series of reactions conventionally summarized by the equation

$6 CO_2 + 6 H_2O + 675$ K cals →

$\qquad\qquad C_6H_{12}O_6 + 6 O_2$ ....(11)
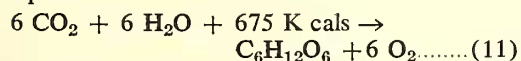
The energy absorbed is supplied by the light.

The mechanism of this process is extremely complicated and is by no means fully understood. For a given plant the rate of production of oxygen depends upon the conditions of illumination, the concentration of carbon dioxide and on other physical variables such as temperature and turbulence. It is also a function of many physiological factors responsible for varied and as yet unpredictable phenomena such as resting, fatigue, aging, inhibition, adaptation and the like. The difficulties encountered in studies of the kinetics of such a complex process in living organisms can hardly be exaggerated, and indeed doubts have often been expressed as to the possibility of deriving significant kinetic relationships. Nevertheless, at least for short periods, the rate of photosynthesis appears to remain constant in a constant environment, and it is proposed to illustrate the influence of the process on the balance of oxygen in an aquarium under such conditions.

With both the two main variables, light and carbon dioxide, a saturation level is reached above which increasing the intensity or concentration causes no change in the rate of photosynthesis, which is at a maximum with respect to these two factors. Measurements of maximum photosynthetic activity recorded in the literature relate to conditions in which at least by intention neither light nor carbon dioxide was limiting. We shall consider the effect due to an aquatic plant of tropical origins, *Valisneria spiralis* (commonly found in indoor aquaria in the United Kingdom and elsewhere), leaves of which, 30 cm. in length, were observed to produce 0.63 mg. oxygen per hour per leaf during daylight (Manning, Juday & Wolf, 1938). Assuming the leaves to be about 1 cm. wide, this rate of production is equal to about 2 mg. O_2/h., 100 cm.^{2}, which is within the range of values $1.3 - 7$ mg. O_2/h., 100 cm.^{2} observed for other aquatic plants (Rabinowitch, 1951, p. 961).

In addition to producing oxygen when illuminated, the living plant is, of course, continuously respiring and for any given conditions the ratio of respiration to photosynthesis governs the level of oxygen in an aquarium. On the average the *rate* of respiration appears to be about 5-15 per cent. of photosynthesis, according to Rabinowitch (1951, p. 7) and Verduin (1952). For detailed information on photosynthesis the reader is referred to the standard text on the subject by Rabinowitch (1951).

Let us suppose the aquarium contains 70 leaves of *Valisneria spiralis*, producing oxygen at a constant rate of 0.63 mg. O_2/h., leaf during daylight and consuming oxygen by respiration at about 10 per cent. of this rate. Then $K_2 = 0.04$ p.p.m./h. and $K_3 = 0.44$ p.p.m./h. (The total volume of water is taken to be 100 litres, as before.)

Case I. If the rate of aeration was small (K $= 0.05/h.$) and the water was initially

saturated with oxygen, then with the aquarium always in darkness (*i.e.*, $K_3 = 0$), the dissolved oxygen would fall toward an equilibrium value of 2 p.p.m. (Equation 5) in accordance with curve ABHI (Text-fig. 3) which has been deduced from Equation (7).

Case II. If on the other hand, the aquarium was continuously illuminated and initially saturated with oxygen, it would become supersaturated, the concentration varying in accordance with curve AJ (Text-fig. 3), reaching an equilibrium value, $C = 10.8$ p.p.m., given from Equation (5) by

$$\frac{dC}{dt} = 0 = 0.05 \ (10-C) - 0.36 -$$
$$0.04 + 0.44.$$

It should be noted that in this case an increase in the rate of aeration, K, to, say, 0.5/h., would reduce the degree of supersaturation to the equilibrium concentration $C = 10.08$ p.p.m. If the concentration of dissolved oxygen was initially less than the saturation value, then upon continuous illumination it would approach the equilibrium value along a curve of the type BCFG (Text-fig. 3).

Case III. Considering a more typical day and night cycle, if the water was initially saturated, then during eight hours' darkness the dissolved oxygen would fall to about 7.4 p.p.m. in accordance with curve AB (Text-fig. 3), deduced from Equation (7), but would recover during daylight to 9.2 p.p.m., to fall again at night to 6.9 p.p.m. Finally an equilibrium would be established in which the maximum concentration, C_D, during daylight and the minimum concentration, C_N, during the night would be given by the simultaneous equations,

$$\log_e \left(\frac{K(C_s - C_D) - K_1 - K_2}{K(C_s - C_N) - K_1 - K_2} \right) = Kt_1$$
$$\text{...(12)}$$

$$\log_e \left(\frac{K(C_s - C_N) - K_1 - K_2 + K_3}{K(C_s - C_D) - K_1 - K_2 + K_3} \right)$$
$$= Kt_2 \text{.......................................(13)},$$

where $t_1 = 8$ hours (darkness), $t_2 = 16$ hours, and the other symbols have the same significance and values as before. Thus $C_D = 8.9$ p.p.m. and $C_N = 6.6$ p.p.m. Therefore the addition of plants to the water under these conditions prevents the concentration of dissolved oxygen from becoming dangerously depleted.

It is not the case, however, that adding plants to an aquarium will necessarily improve conditions for fish. In certain circumstances the concentration of oxygen may fall during the night below the equilibrium (minimum) concentration C_E, attained in the absence of plants. This would be undesirable if, as a result, the concentration fell below the minimum that could be tolerated by the fish. By combining the equation

$$C_E = C_s - K_1/K \text{..............(14)}$$

with Equations (11) and (12), the relation between C_E and C_N becomes

$$C_N = C_E + K_3/K \ [(1 - e^{Kt_2})/(1 - e^{24K}) - K_2/K_3] \text{............(15)}$$

where $C_N, C_E \geqslant 0$.

Thus, $C_N \geqslant C_E$, provided that $(1 - e^{Kt_2})/(1 - e^{24K}) \geqslant K_2/K_3$. The variation of the function $(1 - e^{Kt_2})/(1 - e^{24K})$, which for convenience will be denoted as F, with the over-all absorption coefficient, K, for three different values of the period of illumination, t_2, is shown graphically in Text-fig. 4(a). It will be seen that when the over-all absorption coefficient, K, exceeds the values 0.28, 0.19, and 0.12 (according as $t_2 = 16$, 12 or 8 hours), the function F becomes less than 0.1 and therefore, if, as we have assumed $K_2/K_3 \cong 0.1$, the expression $(F - K_2/K_3)$ becomes negative, so that the minimum concentration during darkness, C_N, falls below C_E.

It will also be evident that for any given value of K, the tendency for C_N to exceed C_E increases as the period of illumination increases, which is perhaps obvious without mathematical derivation. On the other hand the conclusion that the tendency for C_N to fall below C_E increases with increase in the absorption coefficient for solution of oxygen from the air, may at first sight appear more surprising. This arises, however, because for given values of K_1, K_2, and K_3, as the absorption coefficient is increased, the level of the dissolved oxygen concentrations approach nearer to the saturation value, and the amount of oxygen dissolved from the air during daylight may be small by comparison with that dissolved when, although the absorption coefficients are lower, the oxygen deficits are higher and *in proportion* are not reduced so much by the oxygen liberated in photosynthesis. Thus there is not so much opportunity to build up a "reserve" of dissolved oxygen when the absorption coefficient is high, so that when illumination ceases, the dissolved oxygen concentration may quickly fall below the equilibrium value, C_E, that would have been attained in the absence of plants. However, by the same token, as the concentration of dissolved oxygen falls, the oxygen deficit, and hence the rate of solution of oxygen, increases much more rapidly, in proportion, when the absorption coefficient is high than when it is low and the deficits are much greater, so there is less tendency for C_N to fall so far below C_E, when K is high. Substitution of the values for

factor, F, from Text-fig. 4(a) in Equation (15) will show that, for given values of t_2, K_1, K_2, and K_3, as K is increased above the "critical values" at which $C_N = C_E$, then the difference $C_E - C_N$ at first increases (since the factor F decreases and $[F - K_2/K_3]$ increases) but then rapidly begins to decrease, since for values of $K > 0.5$, F becomes negligibly small and Equation 15 reduces to

$$C_E - C_N \cong 0.1 \, K_3/K \ldots\ldots(15a).$$

It will also be seen from Equations (15) and (15a) that the difference, $C_E - C_N$, which is positive or negative depending on the value of K, increases directly in proportion to K_3, the rate of photosynthesis. For instance for $t_1 = t_2 = 12$ hours, $K_2/K_3 = 0.1$, $K = 0.1$, C_N exceeds C_E by 1 p.p.m., for $K_3 = 0.75$ p.p.m./h. and K_3 must be increased by 0.75 p.p.m./h. for each increase of 1 p.p.m. in the difference $C_N - C_E$. On the other hand, for $t_1 = t_2 = 12$ hours, $K_2/K_3 = 0.1$, $K = 0.5$, C_N falls below C_E by 1 p.p.m. when $K_3 \cong 10K \cong 5.0$

p.p.m./h., and for each increase of 1 p.p.m. in the difference, $C_E - C_N$, K_3 must be increased by 5.0 p.p.m./h. For the conditions cited in the example in Case III above we had $C_N - C_E = 3.8$ p.p.m. To make $C_N - C_E = 5$ p.p.m., say, it would be necessary to increase K_3 to 0.61 p.p.m./h.; that is, to increase the number of leaves of *Valisneria spiralis* from 70 to about 97.

To summarize, the major conclusion that may be drawn from the preceding discussion is that it is inadvisable to attempt to improve conditions in an aquarium having a moderate rate of solution from the air ($K \cong 0.3$ to 0.5) in combination with a relatively high rate of absorption by fish, by introducing a high rate of photosynthesis, since under these conditions the dissolved oxygen will fluctuate quite widely about an already low level and may well fall below the tolerance level at night.

Of course, it may be that fish can withstand and thrive in conditions in which the dissolved oxygen falls below the tolerance level for short
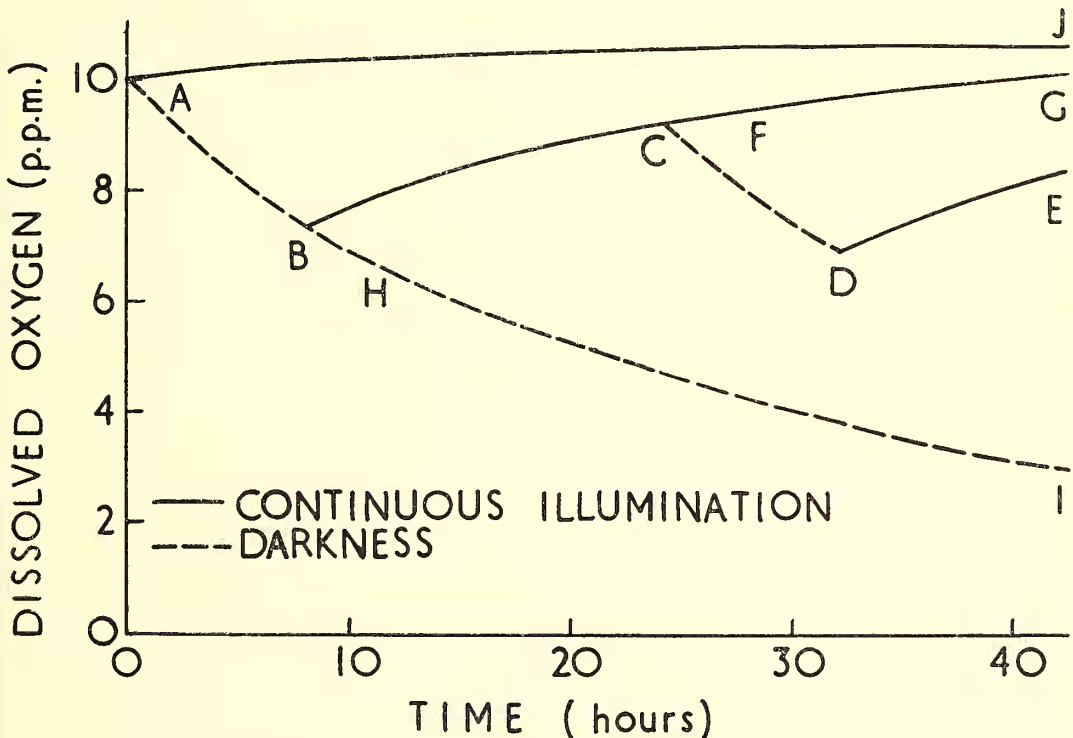
TEXT-FIG. 3.   Effect of the respiration of fish and plants and the production of oxygen by photosynthesis on the concentration of dissolved oxygen in an aquarium.

Over-all absorption coefficient, K = 0.05/h.

Rate of consumption of dissolved oxygen:

by fish, $K_1 = 0.36$ p.p.m./h.,
by plants, $K_2 = 0.04$ p.p.m./h.

Rate of production of dissolved oxygen by photosynthesis: $K_3 = 0.44$ p.p.m./h.

periods but in which the daily average concentration is relatively high. Under such circumstances, the effect of introducing plants could be expressed in terms of the difference between C_E and the average concentration, C_A, given by $C_A = (C_N + C_D)/2$. (The true "time-average" concentration is rather complicated to work out but will not be greatly different from C_A.) The relation between the two can be shown to be

$$C_A = C_E + K_3/K \left[1/2 \left(F_1\right) - K_2/K_3\right]$$
$$\dots\dots\dots\dots\dots\dots\dots\dots(16),$$

where $F_1 = (1 - e^{Kt_2})(1 + e^{Kt_1})/(1 - e^{24K})$. The variation of the numerical values of F_1 with variation in K, for three different values of t_2, is shown in Text-fig. 4(b). It will be seen that if $K_2/K_3 = 0.1$, $C_A > C_E$ under all conditions, since $F_1 > 0.1$, and $C_A - C_E$ may be increased by increasing t_2 or K_3. For $t_2 = t_1 = 12$ hours, $K_2/K_3 = 0.1$, then $C_A = C_E + 0.4 \, K_3/K$ ....(17)

so that to make $C_A - C_N = 1$ p.p.m., we must make $K_3 = 2.5$ K.

LIMITATIONS TO THE KINETIC EQUATIONS FOR PHOTOSYNTHESIS

In addition to the assumption already referred to on page 132, the kinetic equations for aquaria demand that (i) the water remains in the aquarium long enough for equilibrium to be established, (ii) that photosynthesis is independent of the degree of agitation of the water, (iii) that all the oxygen evolved is absorbed by the water, and (iv) that photosynthesis may be varied without restriction by changing the number or size of plants. These assumptions will be briefly considered:

(i). In a crowded aquarium, accumulation of noxious metabolic products may make frequent replacement of water necessary. In a sparsely populated aquarium or pond biochemical self-purification may considerably reduce the frequency with which replacement becomes necessary.

(ii). There appears to be no doubt that the rate of photosynthesis of aquatic plants depends upon the turbulence of the water, because of its effect on the rate of transport of carbon dioxide to the cells (Rabinowitch, 1951, Chapt. 27). Unfortunately, there appears to be little quantitative work on this subject, so for the present it must simply be noted as another variable to be considered.

(iii). When the rate of photosynthesis is high, oxygen may be liberated from the surface of aquatic plants in bubbles. The proportion of the liberated oxygen absorbed into the water will be a function of many factors, but it is doubtful if there is yet sufficient information to take this effect into account in aquaria.

(iv). In a given aquarium, the maximum rate of photosynthesis must inevitably depend on (a) the intensity of illumination and (b) the concentration and rate of supply of carbon dioxide.

(a). *Light intensity.*

It will be seen from Equation (11) on page 135 that 3.5 K cal. of energy are absorbed during the production of 1 gm. of oxygen. For a rate of production of oxygen of 1 p.p.m./h. (*i.e.*, $K_3 = 1.0$) in an aquarium, the equivalent rate of absorption of energy is about 84 gm. cal./litre, day. The daily amount of solar energy incident on a horizontal surface at sea level, of wave lengths which can promote photosynthesis and penetrate a smooth water surface, has been estimated by the U.S. Weather Bureau (Oswald & Gotaas, 1955). At latitude 52° the estimated monthly average amount of radiation in clear weather varies during the year from 21 gm. cal./cm.², day in December to 296 gm. cal./cm.², day in June; the corresponding average values for cloudy conditions are 4 and 176 gm. cal./cm.², day. If we consider a litre of water contained in a 10 cm. cube of glass the surface area will be 600 cm.², and assume that all this area receives radiant energy and neglect any absorption by the glass, the total amount of energy passing into the water will vary during the year from 21×600 to 196×600 gm. cal./day in bright weather, and from 4×600 to 176×600 gm. cal./day in cloudy weather. It has been calculated, however, that only some 2.0 per cent. of visible light incident on aquatic plants is utilized in photosynthesis (Rabinowitch, 1951, p. 1003), so that the net available energy for photosynthesis would vary during the year, taking the two extreme values, between $4 \times 600 \times 0.02$ and $296 \times 600 \times 0.02$ gm. cal./day, 10 cm. cube. If it is assumed that this energy is absorbed during 8 hours of daylight in December and 12 hours of daylight in June, the equivalent maximum rates of production of oxygen would be $3 \times 4 \times 600 \times 0.02/84 = 1.71$ p.p.m./h. and $2 \times 296 \times 600 \times 0.02/84 = 85$ p.p.m./ h. However, the 10 cm. cube would be more similar in size to a gold-fish bowl rather than the average aquarium for which, as the size increased, the ratio of the surface area to volume would decrease, and also therefore the rate of increase of the concentration of dissolved oxygen. For instance, in an aquarium of the size of a 1 m. cube, the ratio of surface to volume would be only 1/10 that in the 10 cm. cube, and in consequence, other things being the same, the corresponding rates of production of oxygen would be 0.171 and 8.5
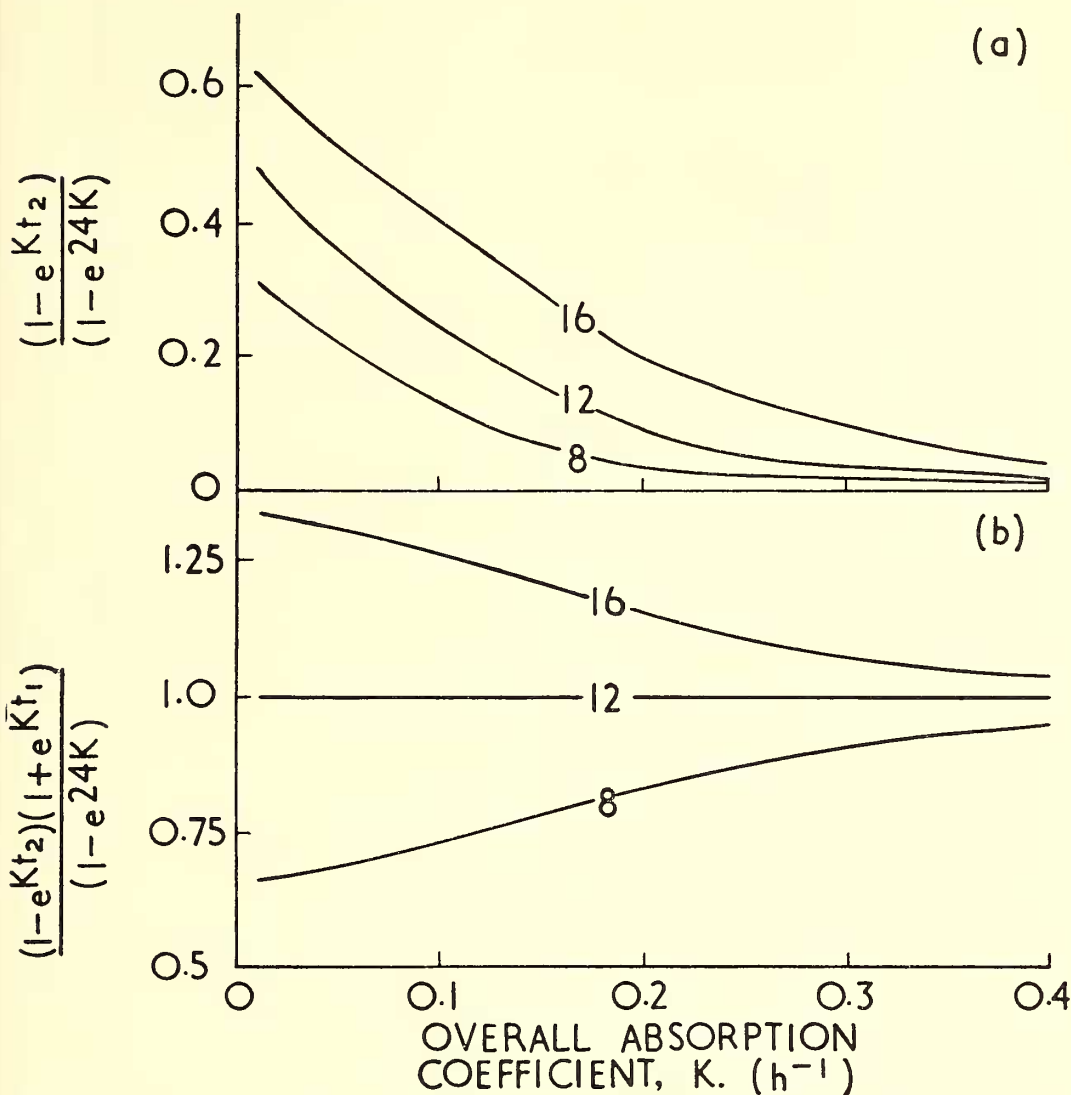
TEXT-FIG. 4. Values of functions in kinetic equations for photosynthetic production of oxygen. Period of daylight illumination, t_2, in hours shown against each curve.

(a) Variation of $\dfrac{1 - e^{Kt_2}}{1 - e^{24}}$ from the equation

$$C_N = C_B + \frac{K_3}{K}\left[\frac{1 - e^{Kt_2}}{1 - e^{24K}} - \frac{K_2}{K_3}\right]$$

with K and t_2.

(b) Variation of $\dfrac{(1 - e^{Kt_2})\,(1 + e^{Kt_1})}{(1 - e^{24K})}$ from the equation

$$C_A = C_B + \frac{K_3}{K}\left[\frac{1}{2}\left\{\frac{(1 - e^{Kt_2})\,(1 + e^{Kt_1})}{(1 - e^{24K})}\right\} - \frac{K_2}{K_3}\right]$$

with K and t_2.

p.p.m./h. In fact, however, the absorption of light by turbidity in the water and other "shading" effects would tend also to increase with increase in size (particularly with increase in depth), so that the actual practical values would be still further reduced. Despite this, it would appear that there is sufficient incident solar energy to support quite high rates of photo-

synthesis in summer, but that in winter, if one relies on daylight to provide energy, the maximum rate of photosynthesis is severely limited.

Carbon dioxide.

It is said that aquatic plants can assimilate carbon dioxide only in the form of neutral molecules, but there is also a possibility that in some cases bicarbonate ions may be utilized, although this contention has given rise to considerable controversy (Rabinowitch, 1951, Chapt. 27). According to Rabinowitch, the saturation level for carbon dioxide in photosynthesis occurs at concentrations in the range $1 - 10 \times 10^{-5}$ Molar, that is, $0.44 - 4.4$ p.p.m.

Carbon dioxide is supplied to the aquarium by (i) absorption from the atmosphere, (ii) the dissociation and hydrolysis of bicarbonate and carbonate ions, and (iii) the respiration of fish and plants. The concentration and distribution of carbon dioxide between its various forms is governed by the constants of the following equilibria:

$$k_s = 0.827 \qquad k_{H_2O} = 10^{-3} \times$$
$$CO_2(g) \quad \rightleftharpoons \quad CO_2(aq) \quad \rightleftharpoons$$
$$2.2 \qquad k_1 = 1.8 \times 10^{-4} \qquad k_2 =$$
$$H_2CO_3 \qquad \rightleftharpoons \qquad H^+ + HCO_3^-$$
$$5.61 \times 10^{-11}$$
$$\rightleftharpoons \quad 2H^+ + CO_3^{--}.$$

N.B. Usually the apparent first dissociation constant, k_1', of carbonic acid is quoted as $k_1' =$

$$\frac{[H^+] \ [HCO_3^-]}{[CO_2] + [H_2CO_3]} = 4.54 \times 10^{-7}.$$

If distilled water is allowed to come into equilibrium with normal air, it will be found to contain approximately 0.4 p.p.m. neutral carbon dioxide molecules (henceforth referred to as "free CO_2") and about 0.08 p.p.m. combined carbon dioxide present as bicarbonate ions. Owing to the small values of the constants k_{H_2O} and k_2, the quantities of carbonic acid and normal carbonate ion are negligible. Natural waters in equilibrium with normal air also contain about 0.4 p.p.m. free CO_2, but the amounts and proportion of combined carbon dioxide in the form of bicarbonate or carbonate ions depend on the pH value and alkalinity of the water. Since the concentration of free CO_2 is close to the lowest estimate of the saturation concentration for photosynthesis, it must be expected that removal of free CO_2 will tend to bring about a decrease in the rate of photosynthesis unless other factors are limiting. However, removal of free CO_2 will displace the CO_2-equilibrium and cause ionized carbon dioxide to recombine to form carbonic acid which dissociates to free CO_2, and additional carbon

dioxide then dissolves from the air. This "resistance" to changes in carbon dioxide concentration, and hence to changes in the rate of photosynthesis, will increase with increase in the total combined carbon dioxide concentration, but will be governed by the rate at which the reactions influencing the equilibria take place; that is, by the rate at which carbon dioxide is made available by the processes (i), (ii) and (iii) above.

(i). If the exit coefficient for carbon dioxide is approximately the same as that for oxygen (a reasonable assumption for natural waters or tap waters but not necessarily for very alkaline solutions), then the maximum rate of supply of carbon dioxide from the air will be K times the equilibrium concentration of free CO_2, i.e., 0.4K p.p.m./h. Therefore, unless the rate of aeration is relatively large, the supply of carbon dioxide from the air will not support a very high rate of photosynthesis.

(ii). When free CO_2 is removed from the system, it can be replaced by the dissociation of carbonic acid and, it is said, bicarbonate ion (Rabinowitch, 1951, Chapt. 27) in accordance with the reactions

$$k_A = 10/sec.$$
$$H_2CO_3 \quad \rightleftharpoons \quad H_2O + CO_2$$
$$k_B = 0.47 \times 10^{-4}/sec.$$
$$HCO_3^- \quad \rightleftharpoons \quad OH^- + CO_2.$$

For a water in equilibrium with the air, the concentration of carbonic acid is $0.4k_{H_2O} = 0.4 \times 2.2 \times 10^{-3} = 8.8 \times 10^{-4}$ p.p.m. Assuming that the reactions $H^+ + HCO_3^- \rightarrow H_2CO_3$ and $H^+ + CO_3^{--} \rightarrow HCO_3^-$ are virtually instantaneous, the maximum rate of supply of carbon dioxide from this source is therefore $8.8 \times 10^{-4} k_A$ p.p.m./sec. = 31.6 p.p.m./h.

The maximum rate of supply from the dehydration of bicarbonate ions will be $0.47 \times 10^{-4} \times 3.6 \times 10^3$ p.p.m./h., p.p.m. $HCO_3^- = 0.169$ p.p.m./h., p.p.m. HCO_3^-. Thus for a concentration of bicarbonate of 100 p.p.m. this corresponds to a rate of supply of 16.9 p.p.m./h.

These rates will tend to fall as carbon dioxide is removed from the system, since apart from the fall in the total concentration of carbon dioxide, the pH value will rise and in consequence the proportions of carbonic acid and bicarbonate will decrease. Ultimately if this trend continues and the water contains calcium ions, calcium carbonate will be precipitated so that some of the combined carbon dioxide hitherto available for photosynthesis will be effectively lost from the system. In a natural water containing an average concentration of combined carbon dioxide of the order of 100 p.p.m. or more, these changes will come about

slowly, and reasonably high rates of photosynthesis should be feasible for long periods. In distilled water, however, changes in the concentration of carbonic acid and bicarbonate ion will be directly proportional to the loss of carbon dioxide from the system, and since the total concentration initially present in water in equilibrium with the air is only about 0.5 p.p.m., even a comparatively low rate of photosynthesis may soon be restricted for lack of carbon dioxide.

Taking all these factors into account, it would seem reasonable to expect the supply of carbon dioxide from ionic dissociation to support continuously a rate of photosynthesis of at least $K_3 \cong X/24t$ p.p.m./h. where X p.p.m. is the total concentration of carbon dioxide in all forms and t is the period between replacement of the water, provided that other factors are not limiting and that K_3 does not exceed a value $K_3 \cong 31.6 + 0.169 \ [HCO_3^-]$ p.p.m./h.

(iii). Fish and the plants themselves are the main respiring organisms to be considered in the aquarium. Since the respiratory quotient for fish is about $0.7 - 1.0$ and one volume of oxygen is liberated per volume of carbon dioxide absorbed in photosynthesis, the maximum rate of photosynthesis from carbon dioxide produced from fish absorbing oxygen at K_1 p.p.m./h. will be $K_3 \cong 0.7 - 1.0K$. Plants will provide carbon dioxide at a rate K_2 equal to the rate of respiration.

If now we assume that the limiting rate of photosynthesis, K_3^L, in aquaria due to restriction in the supply of carbon dioxide is given by the sum of the individual maximum rates of supply due to (i), (ii) and (iii) above, we have

$$K_3^L = K_1 + K_2 + 0.4K + \frac{X}{24t}.$$

Thus if K, K_1, and K_2 take the values 0.05, 0.36, 0.04 as in previous examples, X = 240 p.p.m. (a reasonable value for tap water or natural fresh water) and t = 5 days we have

$$K_3^L = 0.36 + 0.04 + 0.4(0.05) +$$
$$\frac{240}{24 \times 5} = 2.42 \text{ p.p.m./h.}$$

It will be noticed that although this rate is somewhat lower than the limiting rate for summer conditions, it is somewhat greater than the calculated limiting rate of photosynthesis caused by the low level of daylight illumination in winter. Thus the indication from these approximate calculations is that the maximum rate of supply of oxygen by photosynthesis may under some circumstances in the summer be limited by the supply of carbon dioxide rather than the intensity of illumination.

More Complex Systems

The only systems considered have been those in which the absorption or production of oxygen, apart from that due to atmospheric aeration, was a linear function of time and was independent of other variables. There is, however, no *a priori* reason for this other than shortage of detailed information about photosynthesis and respiration, and it should be possible to formulate equations representing the variation of dissolved oxygen with time, if, as information accumulates, these factors prove to be more complicated functions. As a simple example of a more complex system (in the mathematical sense, that is), we may consider the case in which the water in the aquarium has a biochemical oxygen demand (B.O.D.) exerted at a rate such that

$$L_t = L_0 e^{-kt} \dots \dots \dots (18),$$

where L_0 and L_t are the ultimate B.O.D.'s at times 0 and t hours and k is the velocity constant. This situation may well occur in work on the toxicity of effluents, or in aquaria or ponds in which dying plants are present. If absorption by fish is constant, K_1 as before, and $K_2 = K_3 = 0$, then

$$\frac{dC}{dt} = K(C_s - C) - K_1 - kL_0 e^{-kt} \dots \dots (19)$$

and $C = \dfrac{k}{K - k} L_0(e^{-Kt} - e^{-kt}) +$

$$C_0 e^{-Kt} + \frac{(KC_s - K_1)(1 - e^{-Kt})}{K} \dots \dots (20).$$

In this case, the oxygen concentration would pass through a minimum, C_M, given by

$$C_M = C_s - \frac{(kL_0 e^{-kt_M} + K_1)}{K} \dots \dots (21)$$

at time

$$t_M = \frac{1}{K - k} \log_e \left[\frac{K}{k} - \right.$$
$$\left. \frac{K(C_s - C_0) - K_1(K - k)}{L_0 k^2} \right] \dots \dots (22)$$

before finally reaching an equilibrium given by

$$K(C_s - C) = K_1.$$

Suppose, for instance, that in addition to the consumption of oxygen by fish at a rate $K_1 = 0.36$ p.p.m./h., when the rate of reaeration is 0.05/h. (as in curve AB, Text-fig. 5), the water contains an initial ultimate biochemical oxygen demand, L_0, of 10 p.p.m. and that the velocity constant of the B.O.D., k, takes a value of 0.01/h. (Phelps, 1947). If these values are then substituted in Equations (20), (21) and (22), it will be found that the dissolved oxygen will fall to a minimum concentration of 1.77 p.p.m. in 67 hours before gradually recovering to the
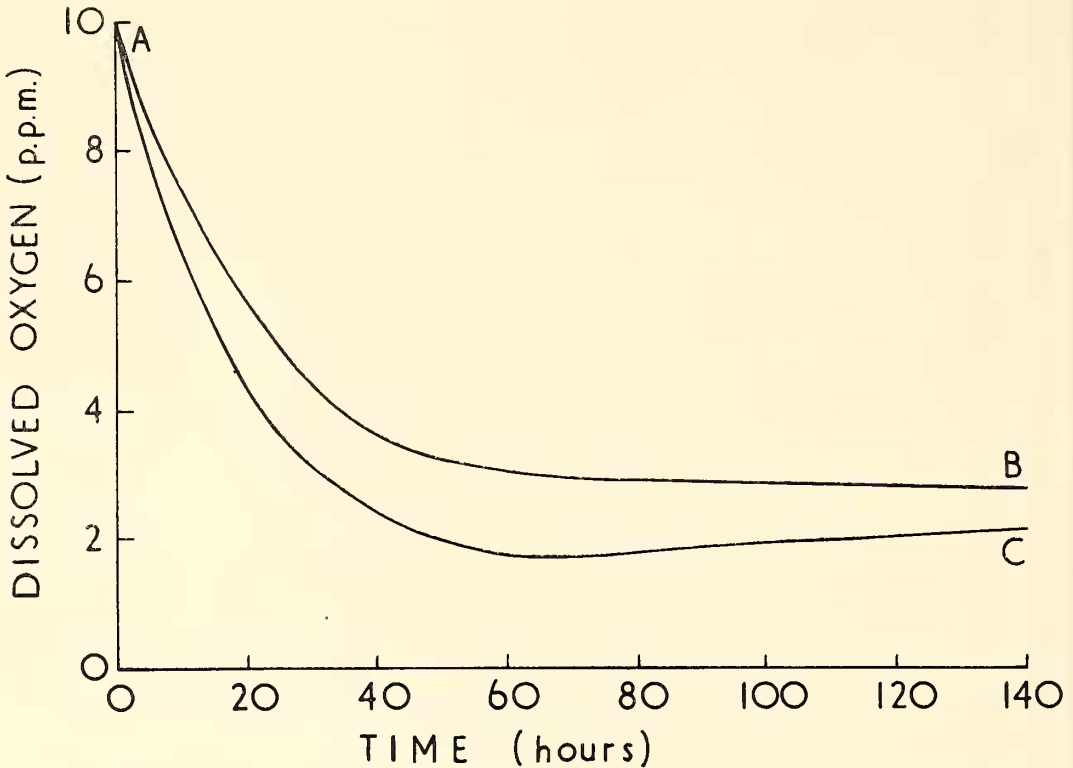
TEXT-FIG. 5. Effect of the respiration of fish and of a biochemical oxygen demand on the variation of concentration of dissolved oxygen in aquaria.

Over-all absorption coefficient, $K = 0.05/h$.

Rate of consumption of dissolved oxygen by fish, $K_1 = 0.36$ p.p.m./h.

Initial ultimate biochemical oxygen demand, $L_0 = 10$ p.p.m.

Velocity constant of B.O.D., k, $= 0.01/h$.

Curve AB: $L_0 = 0$.

Curve AC: $L_0 = 10$ p.p.m.

equilibrium concentration of 2.8 p.p.m. in accordance with curve AC, Text-fig. 5. The chosen value for L_0 is, of course, quite low and could easily be exceeded—for instance in a pond in which there had been a profuse growth of plants during the summer, most of which died and decayed at the onset of colder weather. In such a case, the water might be completely depleted of oxygen and therefore quite unsuitable for fish.

DISCUSSION

Methods for determining the rate of solution of atmospheric oxygen in water and the use of these data in the formulation of simple equations expressing the variation with time of the concentration of dissolved oxygen in aquaria have been described. These equations are based on a number of simplifying assumptions and approximations either because more detailed information is not available or because a more rigorous treatment has not been justified in view of the considerable variability of living organisms. It may well be a chimera to suppose that even with a great deal more information on some of the variable factors, it will be possible to make better than semi-quantitative predictions about variations in the dissolved oxygen content of aquaria, except perhaps in simple systems under rigidly controlled conditions. It is, however, difficult in the present state of knowledge to foresee to what extent more accurate information will be required. Meanwhile it is hoped that the present simple treatment will serve as an introduction to the subject to those who are unfamiliar with the general principles of the "dynamics of aeration," and will also prove a useful starting point

for anyone contemplating a detailed study of the part played by carbon dioxide in aquaria.

ACKNOWLEDGEMENT

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